



Modelling the Concentration Levels of Zinc Chloride Produced by the Release of HC Smoke

Alexander Hill

DSTO-CR-0252

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ABSTRACT

The pyrotechnic smoke known as HC smoke, (a hexachloroethane based obscurant), which is used by the army for training purposes, is produced by the release of the M84A1 artillery projectile. The majority of HC smoke (by weight) is zinc chloride, which is particularly toxic. The smoke was modelled using computer based dispersion models to determine minimum safe downwind distances from the point of release, and approximate dispersion times. A brief explanation of likely atmospheric conditions is given, as well as a summary of the results obtained from the models.

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AQ F02-11-2892

Published by

*DSTO Aeronautical and Maritime Research Laboratory
506 Lorimer St
Fishermans Bend, Victoria 3207 Australia*

*Telephone: (03) 9626 7000
Fax: (03) 9626 7999*

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AR-012-338
June 2002*

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Executive Summary

Smoke munitions have been widely used by the armed forces since the First World War, when US forces employed white phosphorus smoke as an obscurant. The Second World War saw the use of the more effective hexachloroethane based smoke munitions, which produced a thick grey smoke of carbon and zinc chloride. The ability to provide an effective smoke screen to shield units from enemy observation is important, as it can significantly reduce the effectiveness of opposing forces

The Combatant, Protection and Nutrition Branch (CPNB) were requested by the army to model releases of a pyrotechnic smoke used for training purposes. The concern was for the safety of personnel exposed to the smoke, which has been shown to contain toxic compounds. The particular munition of interest is the 105mm M84A1 artillery projectile, which contains a combination of hexachloroethane (HCE), zinc oxide (ZnO) and a small amount of granular aluminium. When the artillery projectile detonates, the smoke that is released, called HC smoke, consists of several toxic compounds; the most abundant of these being zinc chloride

This report details the results of using computer based dispersion models to predict the concentrations of HC smoke at various downwind distances and times. A range of atmospheric conditions is used, in an attempt to subject the results to the full spectrum of possible conditions. Also discussed is the future development of this prediction capability for use by the Australian Defence Force (ADF).

Minimum safe downwind distances and dispersion times were calculated for various atmospheric conditions. Hazard zones varied, but for a release of a single M84A1 round, we can expect minimum safe downwind distances from 180 m to 620 m if released during the day, and from 460 m to 2,750 m for a release at night, depending on the atmospheric conditions. Two other scenarios were also modelled, involving releases of 10 and 20 M84A1 rounds over 10 and 5 minutes respectively. Again, if released during the day, hazard zones of 440 m to 1,600 m are expected, whilst at night a range of 2,500 m to 15,800 m is predicted, depending on the atmospheric conditions. For all scenarios modelled, a release during the day is not expected to contribute to the hazard zones after around 30 mins, whilst it is predicted that at night, it may be necessary to wait more than 8 hours for dispersion, depending on the atmospheric conditions.

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1. Introduction

The Australian Defence Force (ADF) requested modelling of the release of a pyrotechnic smoke used in training. Specifically, the problem consists of three scenarios, each having an associated number of smoke producing artillery projectiles released over a fixed time interval. The major concern of the ADF is the levels of zinc chloride (ZnCl_2) to which its personnel are exposed during training with smoke munitions.

This report provides details of the predicted areas in which specific exposure limits are not exceeded, for a variety of different atmospheric conditions. It does not provide a set of guidelines for safe use of HC smoke munitions, but should be of use to help formulate them.

2. Implementing the Model

The mass of smoke produced for each round of M84A1 artillery is 12.3 lb (~ 5.6 kg), of which approximately 0.6 kg were chlorinated vapours, leaving around 5 kg of particulates. Of the particulates, approximately 80% (by weight) are ZnCl_2 , as discussed in a report [1] and book [2] on HC smoke. For the purposes of this report, only the particulate material is considered, as this is the chief concern of the army (as per advice from Scientific Adviser – Army (SA-A), March 2002).

The smoke was initially modelled using the US Defense Threat Reduction Agency's (DTRA) Hazard Prediction and Assessment Capability (HPAC), under a variety of different conditions, as discussed in Section 2.2, below. HPAC uses a Gaussian puff method known as SCIPUFF to model the dispersion of clouds of particulates/aerosols. This means that, for example, the plume of smoke considered here is modelled as individual puffs of smoke with an associated probability distribution relating concentrations for various points in time and space. For more information on SCIPUFF, see the technical documentation [3].

2.1 Scenarios to be Investigated

Three scenarios were examined, as detailed below:

- **Scenario #1: Single Round**

A single M84A1 artillery round is released, resulting in 5 kg of smoke. This was modelled as an instantaneous release of 5 kg of ZnCl_2 particles, providing a worst-case prediction.

- **Scenario #2: Ten Rounds**

Ten rounds of M84A1 artillery are released, at intervals of one minute. This was modelled as a continuous release of 5 kg per minute of ZnCl_2 particles for ten minutes, for a total release of 50 kg.

- **Scenario # 3: Twenty Rounds**

Twenty Rounds of M84A1 artillery are released, at a rate of two rounds every 30 seconds. This was modelled as a continuous release of 20 kg per minute of ZnCl_2 particles for 5 minutes, for a total release of 100 kg.

2.2 Atmospheric Stability

The dispersion of the smoke was modelled for a range of atmospheric conditions which reflect the stability and turbulent mixing of the atmospheric boundary layer. Stability is largely dependent upon the intensity of incoming solar radiation, cloud cover and the speed of the wind, and is described by the Pasquill stability index. The value of this index ranges from A to F, where A corresponds to extremely unstable (eg. still and hot summer's day), D corresponds to neutral (eg. windy and overcast evening or morning) and F corresponds to extremely stable conditions (eg. a clear night with little wind or cloud cover). A total of five different conditions were used, providing information that covers the spectrum of possible conditions. A description of the parameter values for each stability index is provided in Table 1. For further discussion on Pasquill Stability, DSTO General Document [4] is recommended. Note that the wind speed and cloud cover were held constant throughout the modelling process.

Table 1. HPAC Atmospheric Stability Settings. (Note: Times are local, cloud cover fraction corresponds to the fraction of the sky covered by clouds, and all wind speeds are in metres per second and kilometres per hour).

Pasquill Stability Index	HPAC Weather Settings	
A - Extremely Unstable	Wind Speed	1.5 m/s (5.4 kph)
	Time of Day	10:00 AM
	Cloud Cover Fraction	Clear - 5 %
B,C - Moderately Unstable	Wind Speed	3.5 m/s (12.6 kph)
	Time of Day	10:00 AM
	Cloud Cover Fraction	Scattered - 30 %
D - Neutral	Wind Speed	6 m/s (21.6 kph)
	Time of Day	8:00 AM
	Cloud Cover Fraction	Overcast - 95 %
E - Moderately Stable	Wind Speed	2.5 m/s (9.0 kph)
	Time of Day	12:00 AM
	Cloud Cover Fraction	Broken - 70 %
F - Extremely Stable	Wind Speed	1.5 m/s (5.4 kph)
	Time of Day	12:00 AM
	Cloud Cover Fraction	Clear - 5 %

It is important to note that several climatic factors, such as changes in wind direction, precipitation, terrain roughness and land usage, all provide variations to dispersion. The values chosen, such as constant wind direction, no precipitation and a smooth terrain, all contribute to provide the most conservative, or worst-case scenario, and to keep the results of this study as general and applicable as possible.

2.3 Maximum ZnCl_2 Exposure

After examination of the Material Safety Data Sheet (MSDS) pertaining to ZnCl_2 , exposure standards were found to be as shown in Table 2. In this table, the maximum permissible doses are calculated as the product of the exposure limit (concentration) and the corresponding maximum period for which exposure to this concentration is permitted. For example, Short Term Exposure Limit (STEL) figures correspond to 15 minutes and Immediate Danger to Life/Health (IDLH) figures correspond to 30 minutes. Note that the maximum exposure level for an eight-hour day is also known as the Time Weighted Average (TWA).

Table 2: Exposure Limits for ZnCl_2

	Maximum Exposure For 15 minutes	Maximum Exposure For 8 hour day	Risk to Life and Health After 30 minutes
Exposure Limit	STEL - 2 mg/m ³	TWA - 0.2 mg/m ³	IDLH - 50 mg/m ³
Maximum Permissible Doses	STEL x 15 mins - 1,800 mg-s/ m ³	TWA x 8 hours - 5,760 mg-s/ m ³	IDLH x 30 mins - 90,000 mg-s/ m ³

The MSDS [5] contains more information about the toxicity of ZnCl_2 .

3. Discussion of the Results

3.1 Probabilistic Versus Deterministic Models

HPAC is an inherently probabilistic model, as opposed to many other dispersion models, which calculate dispersion deterministically. In other words, rather than saying that the output is the exact prediction of the model, HPAC says that its output is its best estimate to a certain degree of probability. Whilst for some applications HPAC's "mean" contour (or "most likely" contour) is the most relevant piece of information, it is inappropriate for the stated requirements. When safety of personnel is an issue, as it is here, it may be necessary to require a conditional probability of 99% (or even greater) that the maximum exposure/dose will not be exceeded; in this work a probability of 99.9999% was used.

3.2 Scenario #1 Modelling Results

3.2.1 HPAC Modelling Results

Results of the modelling using HPAC for Scenario #1 were completed first. They showed that with such a small mass of smoke, the cloud had dispersed to a point where its concentrations were no longer hazardous (not significant with respect to increasing dosage) after a period of about 15 minutes; see Appendix A for more details. This meant that the STEL x 15 mins was the binding constraint on the minimum safe downwind distance. In other words, it is not possible with a single round release to exceed the maximum exposure limit for an eight-hour day without already exceeding the STEL x 15 mins. This was true for all atmospheric conditions examined for Scenario #1.

Minimum safe downwind distances varied from 180 metres to 900 metres (taken such that there is less than 0.0001% chance of exposure limits – in this case STEL x 15 mins – being exceeded at this point), depending on the stability conditions. For the full set of distances, see Appendix A.

3.2.2 The Use of a Second Model

These HPAC results were found to be inconsistent with a previous study, as performed by Cichowicz (see [1] & [2]). Cichowicz studied the release of HC smoke that arose from one M5 smoke pot, which contains approximately 31 lb (~ 14.1 kg) of HCE/ZnO. Using extremely stable atmospheric conditions (wind speed of around 1 m/s, clear and at night), and a modelling program known as HAZARD2, Cichowicz estimated that the minimum safe downwind distance was around 3,700 metres. After using HPAC to model a similar quantity of HC smoke, it was found that the HPAC predictions of safe downwind distances were as much as a factor of 4 smaller than those of Cichowicz.

These inconsistencies prompted the use of a second model, known as AUSTOX, which was developed by Monash University's Centre for Applied Mathematical Modelling (CAMP). AUSTOX only models the dispersion of vapour; hence it was necessary to assume that the smoke particulate was neutrally buoyant. This assumption was shown to be appropriate for particulates having the characteristics of HC smoke, since HPAC concentrations of particulates and vapours differed by an average of only 15% over a range of conditions. The climatic data displayed in Table 1, above, was inserted into AUSTOX, and the results calculated. Further details of AUSTOX are available in the technical description of the model [6].

Hazard areas resulting from the AUSTOX model, which provides only deterministic contours, were much larger than those obtained from HPAC, as demonstrated in Table A1 in Appendix A. Note that the HPAC results are the minimum safe distances at a 99.9999% confidence level.

3.3 Scenarios 2 & 3 Modelling Results

Modelling of the multiple release scenarios was completed on both models, with similar trends to the single release scenario above. STEL x 15 mins was again found to be the binding constraint, but the smoke took much longer to disperse (as expected). Time issues became much more important under stable conditions, as the peak doses of 1800 mg-sec/m³ did not always correspond to a minimum safe distance. Due to the slow speed of dispersion in stable conditions, a total dose of more than 1800 mg-sec/m³ can occur outside the minimum safe distance, as the STEL applies only over a 15-minute period (i.e. The dose can take longer than 15 minutes to accumulate, and hence not exceed the exposure limits set out in Table 2). For example, in Scenario #3 with extremely stable conditions, the minimum safe distance was 9 kilometres, but the STEL x 15 mins contour ends at around 11 kilometres. For an illustrated example of this, see Appendix B – Sample HPAC Contour Plots. Consequently, doses over 15 minute intervals from the time of the release were calculated, (until the concentration of smoke had dissipated to insignificant levels), to determine minimum safe distances.

The width of the hazard area is also important. The minimum predicted crosswind distances (relative to directly downwind of the release) to avoid violating the maximum permissible doses set out in Table 2 were also calculated for each of the scenarios. Special care must be taken when interpreting the crosswind distances, as they are heavily reliant on wind speed and direction; small changes in these atmospheric parameters may well alter the width of the hazard area dramatically. Note that to calculate the (predicted) width of the hazard area, minimum crosswind distances need to be doubled.

The differences between AUSTOX and HPAC results are greatest for stable conditions. There is good agreement between the two models for less stable conditions, especially in terms of the time the hazard persisted. Despite the differences of the two models, more stable atmospheric conditions give rise to larger hazard areas and persistence, and increased minimum safe downwind distances, as expected. The results for these scenarios are tabulated in Appendix A.

4. Causes of Discrepancy

So, two well-validated and supported models provide, for the same scenario, significantly different results. It is possible to unearth a number of contributing factors to help shed some light on these discrepancies. For example, AUSTOX does not contain a measure of particle size distributions, so no measure of the various sizes of particles is considered. This means that no account is taken of the settling of the particles. Consequently, AUSTOX is expected to predict larger hazard areas; and this will be more prominent over stable conditions where the dispersion time is much larger. Other factors must contribute to the discrepancy between models, since settling and other phenomena associated with particulates was shown to reduce concentration in the cloud by an average of less than

15%. These factors may include the different ways the two models simulate the atmospheric conditions, such as mean wind speeds, puff merging, time of year, turbulence, etc.

One of the most significant differences in the two models is the way the atmospheric conditions are defined. In AUSTOX, Pasquill Stability is specified explicitly at the start of the release, and does not alter with time, as opposed to HPAC, in which the atmospheric stability is inherent in its calculations. This means that AUSTOX may well be modelling more accurately, but this is reliant on the atmospheric stability remaining stationary for extended periods of time. Since extremely stable conditions occur only on calm, clear nights, it is highly unlikely that stable conditions persist for more than a few hours. HPAC keeps the wind speed and cloud cover constant, but takes into account the effect on stability of changing time. This reasoning provides partial explanation as to why the models differ markedly for stable conditions, but provide similar values for unstable and neutral conditions.

5. Conclusion

Using two modelling capabilities, it has been possible to obtain an interval for predicted minimum safe downwind distances and dispersion times for various atmospheric conditions. For unstable and neutral conditions, the minimum safe distance is expected to be no more than 1,600 metres, and no less than 180 metres, depending on which scenario is being applied and the conditions. After around 30 minutes, the smoke has dispersed to a point that negligible contributions are being made to dosage. For stable conditions, which generally occur at night, there is a greater variation in the results, with safe downwind distances up to 2,750 metres for a single M84A1 round, and from 2,500 to nearly 16,000 metres for the multiple releases. Dispersion times are much greater, ranging from around 1 hour to more than 8 hours.

It should be possible to interpolate these results to obtain a range of expected minimum safe downwind distances for most atmospheric conditions. These intervals are based on worst-case predictions, and need to be recognised as such. It must be emphasized that the atmosphere is very complex, and any model will only be, at best, a prediction of the possible outcome, and is unlikely to have a consistently high degree of accuracy. Nevertheless, this report should be a valuable aid in terms of creating a set of standing orders for the safe use of M84A1 projectiles in training.

Previous studies have predicted hazard zones to lie within the intervals found in this report, however, it has not been possible to examine the model used previously (known as HAZARD2), in detail. At this stage, advice on the most applicable model for this situation is not possible, and future refinements of the hazard zones set out in this report will need to evaluate the validation studies completed on both AUSTOX and HPAC.

Possible future developments of this modelling capability include the ability to provide information on the concentrations of HC smoke (under various atmospheric conditions) that remain visible. This should give users of these smoke munitions a much better indication as to when re-release of HC smoke can safely occur. The creators of HPAC, DTRA, are developing an add-in module for HPAC to predict the obscuration provided by certain smoke munitions, which, in conjunction with the transport and diffusion model SCIPUFF, could be used to model obscuration under real-time conditions. As yet, this capability is still in its prototype phase.

6. References

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- [2] Toxicity of Military Smokes and Obscurants, Volume 1, 1997, National Academy Press, Chapter 5, p 127-160.
- [3] Sykes, R I, et. al. PC-SCIPUFF Version 1.2 PD Technical Documentation, ARAP Report No. 718, 1998, Titan Corporation Research & Technology Division, Princeton, NJ.
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- [5] Zinc Chloride Fume, ChemWatch Material Safety Data Sheet, CHEMWATCH 35288, 2000
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Appendix A: Summary of Modelling Results

A.1. Scenario #1 – Single M84A1 Round

Stability	A	B,C	D	E	F
HPAC Min Dist <small>(99.9999%)</small> ¹	180	260	320	460	900
Hazard-Free Time _(predicted) ²	< 15 min	< 15 min	< 15 min	~ 45 min	~ 60 min
Min Crosswind Dist ³	60	55	40	40	60
AUSTOX Min Dist ⁴	230	420	620	1,250	2,750
Hazard-Free Time _(predicted)	< 15 min	< 15 min	< 15 min	~ 45 min	~ 3 - 4 hrs
Min Crosswind Dist	75	65	60	80	100

A.2. Scenario #2 – Ten M84A1 Rounds

Stability	A	B,C	D	E	F
HPAC Min Dist <small>(99.9999%)</small>	450	520	800	2,500	5,400
Hazard-Free Time _(predicted)	~ 15 min	~ 15 min	~ 15 min	~ 45 min	~ 1 - 2 hrs
Min Crosswind Dist	90	70	55	95	290
AUSTOX Min Dist	440	690	870	3,700	10,500
Hazard-Free Time _(predicted)	~ 15 min	~ 15 min	< 30 min	~ 1 - 2 hrs	> 8 hrs
Min Crosswind Dist	110	80	70	130	350

A.3. Scenario #3 – Twenty M84A1 Rounds

Stability	A	B,C	D	E	F
HPAC Min Dist <small>(99.9999%)</small>	800	850	1,300	5,300	9,000
Hazard-Free Time _(predicted)	< 30 min	< 30 min	< 30 min	~ 1 - 2 hrs	~ 3 - 4 hrs
Min Crosswind Dist	200	120	80	160	590
AUSTOX Min Dist	590	1,050	1,600	5,050	15,800
Hazard-Free Time _(predicted)	< 30 min	< 30 min	< 30 min	~ 3 - 4 hrs	> 8 hrs
Min Crosswind Dist	160	120	100	230	520

Appendix A Notes:

- 1: Minimum safe downwind distances (in metres), as predicted by HPAC with 99.9999% confidence.
- 2: Times at which the models predict the concentrations will be virtually negligible.
- 3: Minimum predicted crosswind distance (in metres) to avoid violating STEL x 15 mins – measured from directly downwind of the release. In other words, the minimum distance to move in a crosswind direction to avoid exceeding STEL if directly downwind (double this for approximate hazard area widths).
- 4: Minimum safe downwind distances (in metres) as predicted by AUSTOX.

Appendix B: Sample HPAC Contour Plots

B.1. Scenario #1, Pasquill Stability F (Stable)

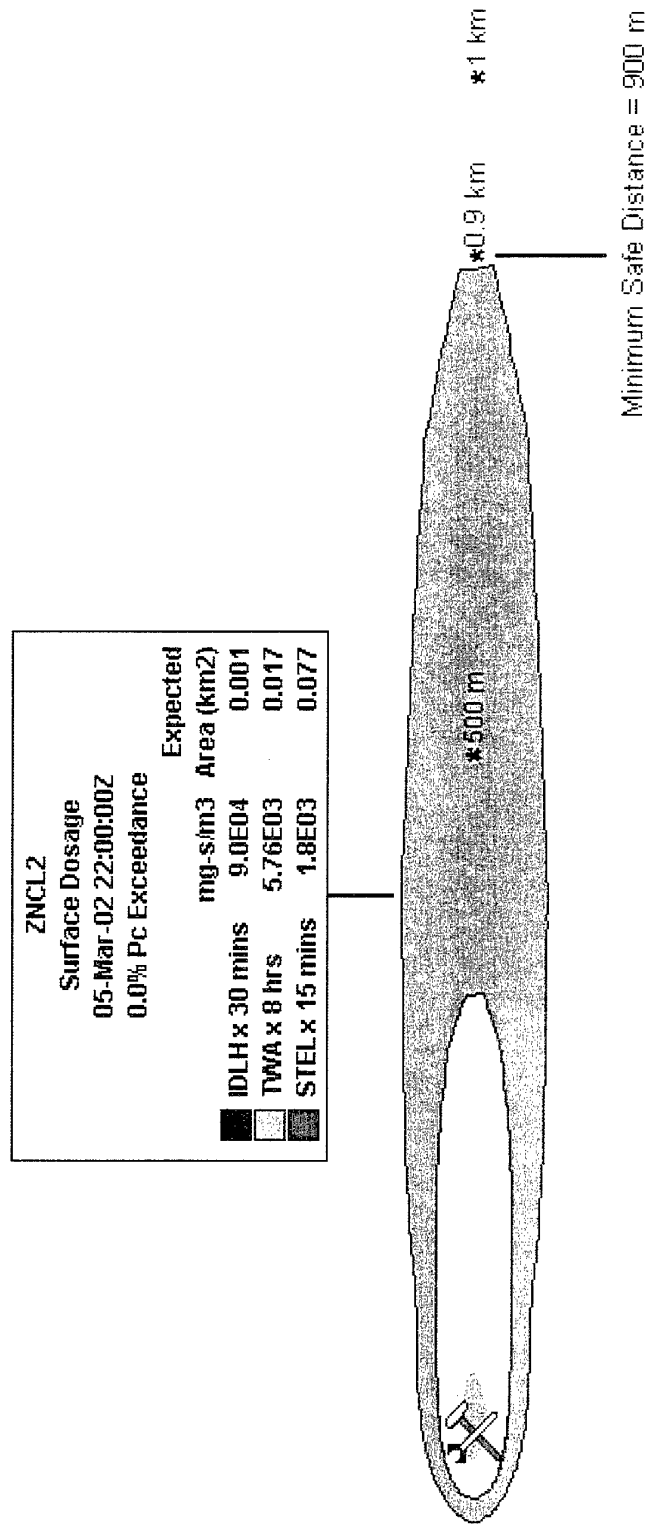


Figure B1: HPAC contour plot for single M84A1 round. Note that minimum distance to receive less than 1800 mg-s/m³ in 15 minutes (STEL) is the same as the minimum distance to receive a total dose that is less than 1800 mg-s/m³ (both ~ 900m).

B.2. Scenario #3, Pasquill Stability F (Stable)

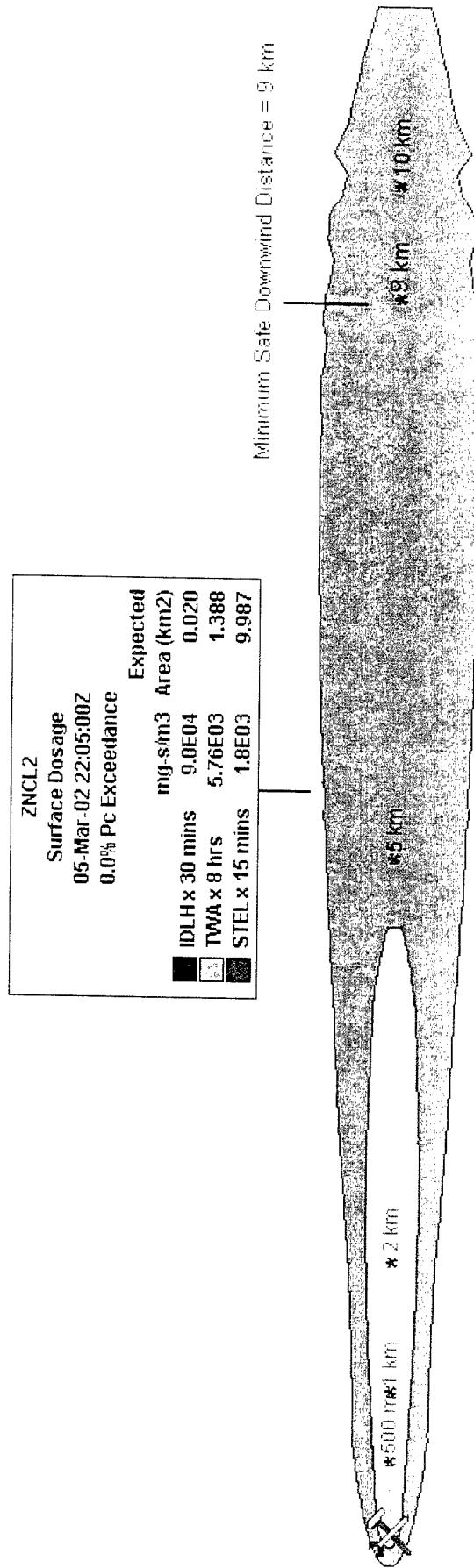


Figure B2: HPAC contour plot for twenty M84A1 rounds. Note that minimum distance to receive less than 1800 mg-s/m³ in 15 minutes (STEL) (9 km) is not the same as the minimum distance to receive a total dose that is less than 1800 mg-s/m³ (~12 km). Also note the change in scale from Figure B1.

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2 TITLE Modelling the Concentration Levels of Zinc Chloride Produced by the Release of HC Smoke			3 SECURITY CLASSIFICATION (FOR UNCLASSIFIED REPORTS THAT ARE LIMITED RELEASE USE (L) NEXT TO DOCUMENT CLASSIFICATION) Document (U) Title (U) Abstract (U)		
4 AUTHOR(S) Alexander Hill			5 CORPORATE AUTHOR Aeronautical and Maritime Research Laboratory 506 Lorimer St Fishermans Bend Victoria 3207 Australia		
6a. DSTO NUMBER DSTO-CR-0252		6b. AR NUMBER AR-012-338		6c. TYPE OF REPORT Client Report	
				7 DOCUMENT DATE June, 2002	
8 FILE NUMBER 510/207/1319	9 TASK NUMBER 99/055	10 TASK SPONSOR ARM		11. NO. OF PAGES 10	12. NO. OF REFERENCES 6
13. URL on the World Wide Web http://www.dsto.defence.gov.au/corporate/reports/DSTO-CR-0252.pdf				14. RELEASE AUTHORITY Head, Combatant Protection and Nutrition Branch	
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19. ABSTRACT The pyrotechnic smoke known as HC smoke, (a hexachloroethane based obscurant), which is used by the army for training purposes, is produced by the release of the M84A1 artillery projectile. The majority of HC smoke (by weight) is zinc chloride, which is particularly toxic. The smoke was modelled using computer based dispersion models to determine minimum safe downwind distances from the point of release, and approximate dispersion times. A brief explanation of likely atmospheric conditions is given, as well as a summary of the results obtained from the models.					